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Picosecond x-ray laser photoelectron spectroscopy of room temperature and heated materials

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Abstract. An 84.5 eV Ni-like Pd ion 4d – 4p x-ray laser source generated by the LLNL Compact Multipulse Terawatt (COMET) tabletop system has been used to probe the electronic structure of various metals and semiconductors. In addition to the ~4 – 5 ps time resolution, the probe provides the necessary high photon flux ($>10^{12}$/pulse), narrow line width ($\Delta E/E \sim 2 \times 10^{-5}$) and coherence for studying valence band and shallow core electronic structure levels in a single shot. We show some preliminary results of room temperature and heated thin foil samples consisting of 50 nm Cu coated on a 20 nm C substrate. A 527 nm wavelength 400 fs laser pulse containing 0.1 – 2.5 mJ laser energy is focused in a large 500 × 700 μm^2 (FWHM) spot to create heated conditions of $0.07 – 1.8 \times 10^{12}$ W cm^{-2} intensity.

1. Introduction

X-ray and EUV induced photoemission spectroscopy (PES) is a powerful surface analysis tool for measuring the electronic structure of matter. The radiation photoionizes the material and the ejected electrons are subsequently detected in a photoelectron spectrometer. Different sources have been used over the years ranging from synchrotrons [1, 2], laser-produced plasmas [3, 4], laser-produced higher order harmonics (HOH) [5 – 7] to x-ray lasers [8]. The main goal has been to develop sources that have a sufficiently large photon number, a mono-energetic line and in a short pulse duration. The major advantage of using the laser-driven sources, particularly the HOH and x-ray lasers, is that the soft x-ray pulse duration can be in the ultrafast regime from below 100 fs to a few ps. This short pulse duration is required to conduct pump-probe experiments at room temperature or materials that have been excited or heated on fast timescales. For example, an optical laser pulse can be used to excite the material while the x-ray beam probes the induced changes. The time resolution in the technique is determined by the intrinsic x-ray pulse duration and over a series of shots the probe can be delayed to study the excited matter evolution [5, 6].

Our objective in recent years has been to achieve improved single-shot PES data based on a pulsed Ni-like Pd ion, $4d – 4p$ 85 eV x-ray laser used in conjunction with electron time-of-flight (eTOF) spectroscopy. The soft x-ray laser has a high photon flux ($>10^{12}$/pulse), 4 – 5 ps pulse duration and narrow line width ($\Delta E/E \sim 2 \times 10^{-5}$). This photon energy has a large photo-ionisation cross-section for valence band and shallow core level

electrons with binding energies up to ~40 eV [9]. We have recently performed pump-probe experiments where the focus now is to extend the technique into dynamic studies of materials. We report on our first results x-ray laser PES data of room temperature and heated thin Cu foils.

2. Experimental Methods and Results

The experimental station at the end of the x-ray laser beam line was recently re-built [10] and a new eTOF spectrometer, designed and fabricated by the University of Nevada Reno group, installed [11]. Figure 1 shows a schematic of the x-ray laser photoelectron

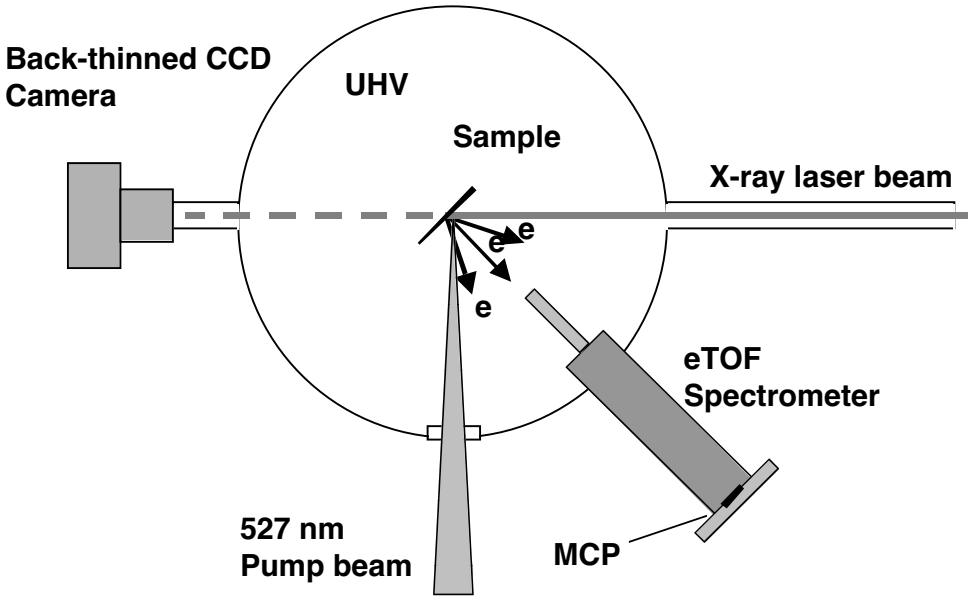

Figure 1. Schematic of x-ray laser photoelectron spectroscopy experimental setup.

spectroscopy experimental setup. The x-ray laser probe beam is collimated by a normal incidence Mo:Si multilayer spherical mirror and relayed along the vacuum beam line by a 45° Mo:Si multilayer flat mirror. The narrow reflectivity window of both mirrors selects the x-ray laser wavelength. A beam block in the x-ray laser chamber also minimizes other plasma x-rays reaching the sample. A pinhole isolates the beam line from the experimental ultra-high vacuum (UHV) chamber, which typically operates below 5×10^{-8} mbar pressure. The x-ray laser is aligned using a back-thinned CCD camera to a cross wire fiducial on the sample manipulator. A fast 400 fs, 527 nm wavelength laser pump beam can be focused and aligned similarly to overlap the two beams onto the sample. The optical pump laser is timed relative to the x-ray laser beam at the sample to within ~5 ps. The pump beam produces rapid heating and depending on the intensity can excite bound electrons, induce phase changes or ionise the sample. The x-ray laser beam can probe the material at various times generating the photoelectrons from the sample surface. These low energy photoelectrons, with K.E. < 84.5 eV, emitted from the valence band and shallow core levels are detected by the e-TOF spectrometer, the operation of which is described in detail elsewhere [11]. The signal is acquired and digitized using a fast 3 GHz oscilloscope. Due to the surface sensitivity of the technique, where the electron escape depth is typically in the range of 0.5 – 2 nm, surface oxidation and contamination are removed by UV ozone cleaning prior to analysis.

The ejected photoelectrons have discrete kinetic energy $E_k = h\nu - E_b - \phi$, where $h\nu$ is the energy of the incident x-ray laser photon (84.5 eV), E_b is the binding energy of the photoelectron relative to the Fermi level. The work function, ϕ, varies for each material and is 4.1, 4.6 and 4.8 eV for Ta, Cu and Ge, respectively (all materials that we have studied). By definition the Fermi level is used as the zero binding energy level. Each photoelectron has a discrete energy representative of the element from which it was emitted thus allowing one to identify the atomic species present. Furthermore, the binding energy of an electron is influenced by its chemical environment and thus can be used to identify the chemical state of a given atom in the sample [4]. Oxide layers in particular are prevalent for many materials. In some cases a scattered x-ray peak may be observed tens of nanoseconds before the photoelectrons and this prompt signal can be used as a timing fiducial. The valence band electrons have the highest kinetic energy and are the first arrival photoelectron signals in the time-of-flight technique. The shallow core levels arrive after the valence band electrons. Another common feature observed is a broad continuum background that originates from secondary electrons from deeper within the material that undergo multiple scattering and generate low energy electrons.

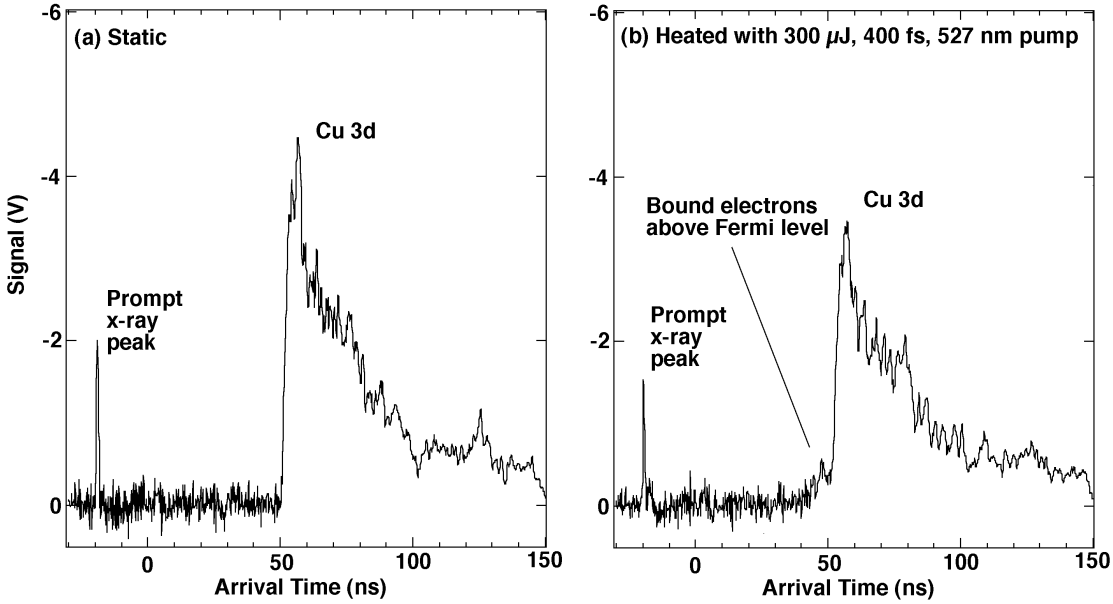

Figure 2.(a) X-ray laser generated photoelectron spectrum of 50 nm Cu on 20 nm C substrate thin foil at room temperature (static). (b) Photoelectron spectrum of same thin foil heated by 300 μJ, 400 fs, 527 nm pump beam focused at 2×10^{11} W cm^{-2} intensity.

Figure 2 is an example of very recent data that was taken from a thin foil sample consisting of 50 nm Cu coated on a 20 nm C substrate. This sample is sufficiently thin to observe the transmitted x-ray laser beam simultaneously with the photoelectron signal. The room temperature or static sample, Fig. 2(a), is shown without the optical heating beam. The peak at -20 ns is from scattered x-ray laser photons being detected by the microchannel plates at the bottom of the drift tube of eTOF spectrometer. The abrupt onset of the first photoelectron signal is recorded at ~50 ns. The peak associated with the Cu 3*d* level is evident in the valence band. The experiment was repeated again with the 400 fs, 527 nm optical pump beam focused onto a large 500×700 μm^2 (FWHM) spot on the same sample. The x-ray laser probe and optical pump were timed to coincide on the sample. Approximately 300 μJ of laser energy corresponding to 2×10^{11} W cm^{-2} intensity was used on this shot. It is noted that the x-ray laser beam overfilled the optical beam on

the sample so that there are detected photoelectron signals from heated and unheated regions of the foil. It is observed that the 3*d* peak intensity has been lowered and there exists a small foot just before the strong onset at ~50 ns. The latter feature is associated with bound electrons above the Fermi level which are being excited by the pump beam. Increasing the pump energy by a further factor of ten generates a strong electron signal before 50 ns that indicates the sample is in an ionized state. These experiments can be repeated by changing the pumping parameters. For example, by controlling the pump energy different states of matter can be studied. Further experiments are ongoing to study the relaxation processes at different time delays between the probe and the pump.

3. Conclusions

In summary, we have shown that picosecond x-ray lasers can be used as a surface analysis probe for metals and semiconductors. The pulsed x-ray source photoionizes the valence band and shallow core level electrons that are subsequently detected in a high resolution electron time-of-flight spectrometer. The first pump-probe experiments have been carried out where an optical laser heats a thin Cu foil sample and excites electrons above the fermi level.

Acknowledgments

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References

[1] R. Z.Bachrach *et al*., *Jn. Vac. Sci. Technol*. **12**, 309 – 312 (1975).
[2] T.E. Glover *et al*., *Phys. Rev. Lett*. **90**, 236102 (2003).
[3] H. Kondo *et al*., *Appl. Phys. Lett*. **69**, 182 (1996).
[4] H. Kondo *et al*., *Appl. Phys. Lett*. **72**, 2688 (1998).
[5] A. Rettenberger and R. Haight, *Phys. Rev. Lett*. **76**, 1912-1915 (1996).
[6] M. Bauer *et al*., *Phys. Rev. Lett*. **87**, 025501-1 (2001).
[7] T. Munakata *et al*, *Surface Science* **532–535**, 1140 – 1144 (2003).
[8] J. Dunn *et al*., *X-ray Lasers 2002*, AIP Conf. Proc. **CP641**, ed. J.J. Rocca, J. Dunn, and S. Suckewer 481 – 488 (2002).
[9] J.J. Yeh and I. Lindau, *At. Dat. Nucl. Data Tabl*. **32**, 1 (1985)
[10] A.J. Nelson *et al*., *Soft x-ray lasers and Applications V*, SPIE Int. Soc. Opt. Eng. Proc, vol. **5197**, ed. E.E. Fill and S. Suckewer, 168 – 173 (2003).
[11] O. Hemmers *et al*., *Rev. Sci. Instrum*. **69**, 3809 - 3807 (1998).